



TITLE:

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AUTHOR(S):

Yoshida, Masato; Wang, Han; Shimbayashi, Takuya; Fujita, Ken Ichi

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Article

Dehydrogenative Transformation of Alcoholic Substrates in Aqueous Media Catalyzed by an Iridium Complex Having a Functional Ligand with α -Hydroxypyridine and 4,5-Dihydro-1*H*-imidazol-2-yl Moieties

Masato Yoshida, Han Wang, Takuya Shimbayashi and Ken-ichi Fujita * 

Graduate School of Human and Environmental Studies, Kyoto University, Kyoto 606-8501, Japan; yoshida.masato.66x@st.kyoto-u.ac.jp (M.Y.); oukan2012@gmail.com (H.W.); shimbayashi.takuya.5z@kyoto-u.ac.jp (T.S.)

* Correspondence: fujita.kenichi.6a@kyoto-u.ac.jp; Tel.: +81-75-753-6827

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Abstract: A new catalytic system that employs water as an environmentally friendly solvent for the dehydrogenative oxidation of alcohols and lactonization of diols has been developed. In this catalytic system, a water-soluble dicationic iridium complex having a functional ligand that comprises α -hydroxypyridine and 4,5-dihydro-1*H*-imidazol-2-yl moieties exhibits high catalytic performance. For example, the catalytic dehydrogenative oxidation of 1-phenylethanol in the presence of 0.25 mol % of the iridium catalyst and base under reflux in water proceeded to give acetophenone in 92% yield. Additionally, under similar reaction conditions, the iridium-catalyzed dehydrogenative lactonization of 1,2-benzenedimethanol gave phthalide in 98% yield.

Keywords: dehydrogenation; iridium catalyst; functional ligand; alcohol; diol; ketone; lactone; water solvent

1. Introduction

From the viewpoint of green sustainable chemistry, it is important to accomplish synthetic organic reactions efficiently using water as a solvent. Because water is incombustible, non-toxic, inexpensive, and easily available in large quantities, it is important that research aims at using water as a solvent for organic synthesis [1–6]; however, it is generally difficult to use water as a solvent in such reactions, especially in reactions that require homogeneous transition metal catalysts. This is probably due to the fact that most homogeneous transition metal catalysts have problems when used in aqueous media, such as (1) instability in water, (2) insolubility in water, and/or (3) inactivity in water. These limitations have prevented the development of methods for catalytic organic synthesis in aqueous media.

Recently, with an objective to overcome the aforementioned problems, we developed a homogeneous dicationic iridium catalyst with a bipyridine-based functional ligand, which is highly soluble and stable in water [7]. Additionally, we reported some catalytic systems that were active for the dehydrogenative oxidation reaction of alcohols in aqueous media, for the production of aldehydes, ketones, carboxylic acids, and lactones [8–10]. These achievements were remarkable as uncommon examples of catalytic organic synthesis using water as a solvent [11–22]; however, some issues remained unresolved such as (1) the necessity of using comparatively large amounts of catalyst, (2) the significant effort required to synthesize the functional ligands, and (3) the limited scope of substrates that can be used as a starting material for the dehydrogenative reactions.

In this study, we synthesized a series of iridium complexes bearing a bidentate functional ligand based on a pyridine and an imidazoline ring. These catalysts were successfully applied to the production of ketones and lactones in water using a small amount of catalyst.

2. Results and Discussion

First, a series of dicationic complexes **1–4** were prepared (Figure 1). Complexes **1** and **2** have bidentate functional ligands that comprise α -hydroxypyridine and 4,5-dihydro-1H-imidazol-2-yl moieties. Complex **3** does not have hydroxy group in the pyridine ring of the functional ligand. Complex **4** includes methoxy group instead of hydroxy group at the α -position in the pyridine ring of the functional ligand. The structures of these complexes **1–4** were determined by NMR data and elemental analyses. For example, in the ^1H NMR analysis of **1** [23], three signals in the aromatic region at δ 8.13, 7.63, and 7.33 ppm, which would be assigned as protons on the pyridine ring, were observed. Additionally, two sets of signals that can be assigned to the methylene protons in 4,5-dihydro-1H-imidazol-2-yl moiety were observed at δ 4.34 and 4.10 ppm as triplet signals with each integration values corresponding to 2H, clearly indicating the bidentate *N,N*-chelating nature of the ligand in complex **1**. Details of the procedures for the preparation of complexes **1–4** and their analytical data are included in the experimental section. All these complexes were highly soluble in water and stable under air or in water for extended periods of time. Therefore, we decided to explore their applications as catalysts for the dehydrogenative oxidation of organic substrates in aqueous media following our previous work on this type of reaction.

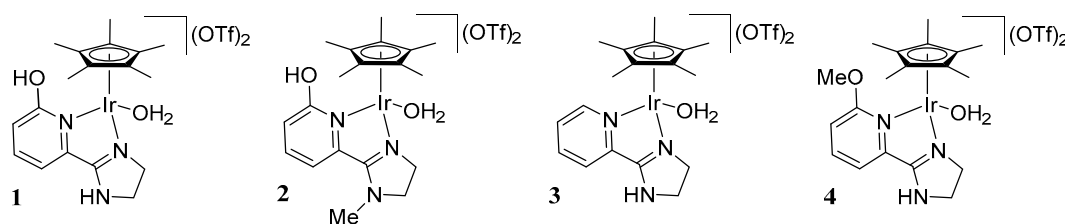


Figure 1. The dicationic complexes **1–4** bearing a bidentate ligand based on pyridine and 4,5-dihydro-1H-imidazole-2-yl moieties.

Thus, we examined the dehydrogenative oxidation of 1-phenylethanol (**5a**) to acetophenone (**6a**) in aqueous media using the water-soluble iridium complexes **1–4**. The results are summarized in Table 1. Complex **1** and **2** having an α -hydroxypyridine moiety in the functional ligand exhibited high catalytic performance, with the activity of **1** slightly higher than that of **2** (entries 1 and 2). High yield of **6a** was accomplished by the employment of a very small amount (0.25 mol %) of both catalyst **1** and Na_2CO_3 (entry 1). The presence of hydroxy group at the α -position of the functional ligand was observed to be indispensable for achieving a high catalytic performance; complex **3** without a hydroxy group and complex **4** with a methoxy group exhibited poor catalytic activity (entries 3 and 4). The importance of hydroxy group at α -position of the pyridine ring in the functional ligand will be discussed later in the explanation of catalytic mechanism (*vide infra*). When compared with our previously reported catalysts for the dehydrogenative oxidation of alcohols in aqueous media, complex **1** can be regarded as one of the most effective catalysts [7,9,24].

Table 1. Dehydrogenative oxidation of 1-phenylethanol (**5a**) to acetophenone (**6a**) in aqueous media using water-soluble iridium complexes **1–4**.

$$\begin{array}{c} \text{OH} \\ | \\ \text{Ph}-\text{CH}-\text{CH}_3 \\ \textbf{5a} \end{array} \xrightarrow[\text{H}_2\text{O, reflux, 20 h}]{\text{cat. [Ir] (0.25 mol \%)} \\ \text{Na}_2\text{CO}_3 (0.25 \text{ mol \%})} \begin{array}{c} \text{O} \\ || \\ \text{Ph}-\text{CH}-\text{CH}_3 \\ \textbf{6a} \end{array} + \text{H}_2$$

entry	cat.	conv. of 5a (%) ^a	yield of 6a (%) ^a
1	1	92	92
2	2	89	89
3	3	14	14
4	4	25	25

^a Determined by GC analysis.

With an optimal catalyst in hand, we further focused on the optimization of basic additive for the dehydrogenative oxidation of **5a** to **6a** catalyzed by **1**. The results are summarized in Table 2. The reaction without any basic additive resulted in a very low yield of **6a** (16%). However, addition of a variety of bases, such as Na₂CO₃, NaOH, NaHCO₃, Li₂CO₃, K₂CO₃, and Cs₂CO₃, considerably improved the catalytic activity of **1**, with the highest yield of **6a** (92%) obtained using 0.25 mol % of Na₂CO₃ (entry 2). We think that the addition of base would lead to the formation of catalytically active monocationic species. The detailed explanation of the effect of base will be discussed later (*vide infra*).

Table 2. Optimization of the basic additive for the dehydrogenative oxidation of **5a** to **6a** catalyzed by **1** in aqueous media.

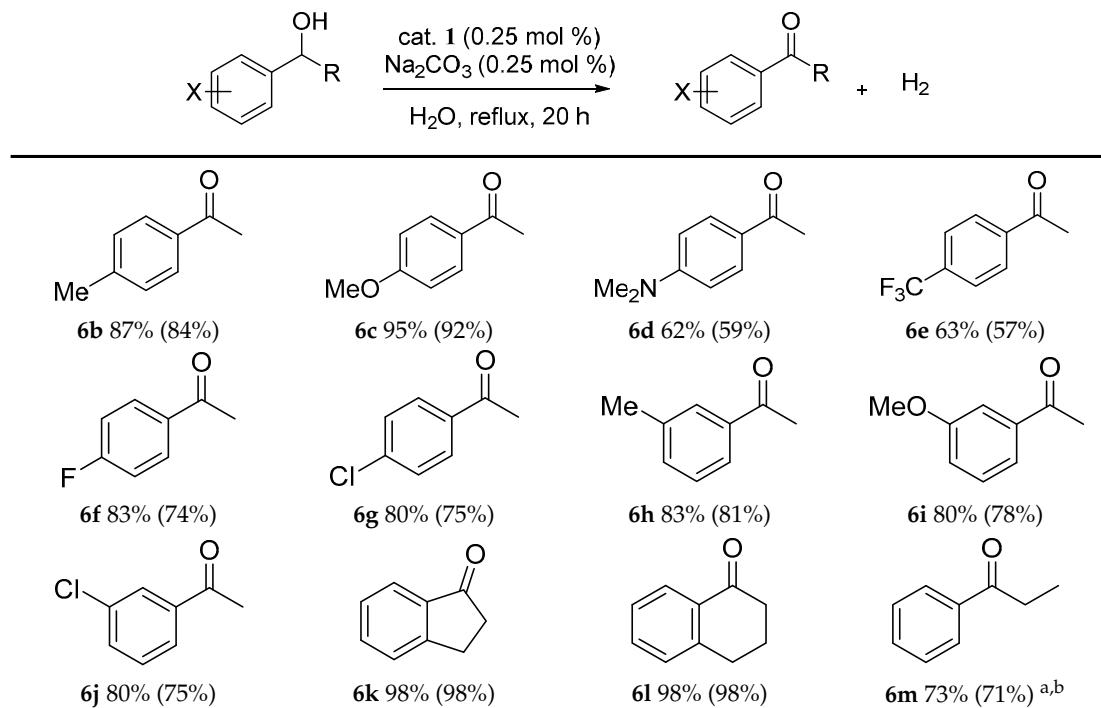
$$\begin{array}{c} \text{OH} \\ | \\ \text{Ph}-\text{CH}-\text{CH}_3 \\ \textbf{5a} \end{array} \xrightarrow[\text{H}_2\text{O, reflux, 20 h}]{\text{cat. } \textbf{1} (0.25 \text{ mol \%}) \\ \text{base}} \begin{array}{c} \text{O} \\ || \\ \text{Ph}-\text{CH}-\text{CH}_3 \\ \textbf{6a} \end{array} + \text{H}_2$$

entry	base (mol %)	conv. of 5a (%) ^a	yield of 6a (%) ^a
1	none	16	16
2	Na ₂ CO ₃ (0.25)	92	92
3	Na ₂ CO ₃ (0.50)	81	81
4	NaOH (0.50)	83	83
5	NaHCO ₃ (0.50)	82	82
6	Li ₂ CO ₃ (0.25)	83	82
7	K ₂ CO ₃ (0.25)	83	83
8	Cs ₂ CO ₃ (0.25)	86	86

^a Determined by GC analysis.

To explore the scope of the new catalytic system that employs **1** and Na₂CO₃ in aqueous media, various secondary alcohols were subjected to the optimized reaction conditions. The results are summarized in Table 3. The reactions of 1-arylethanol bearing electron-donating and electron-withdrawing substituents in the aromatic ring smoothly proceeded to give the corresponding acetophenone derivatives in moderate to high yields. Methoxy, *N,N*-dimethylamino, trifluoromethyl, fluoro, and chloro groups were tolerated in this catalytic system. 1-Indanol and 1-tetralol were also converted into the corresponding ketones in excellent yields. Additionally, 1-phenyl-1-propanol could be dehydrogenatively oxidized to propiophenone, even though a relatively higher catalyst loading and longer reaction time were required in this case.

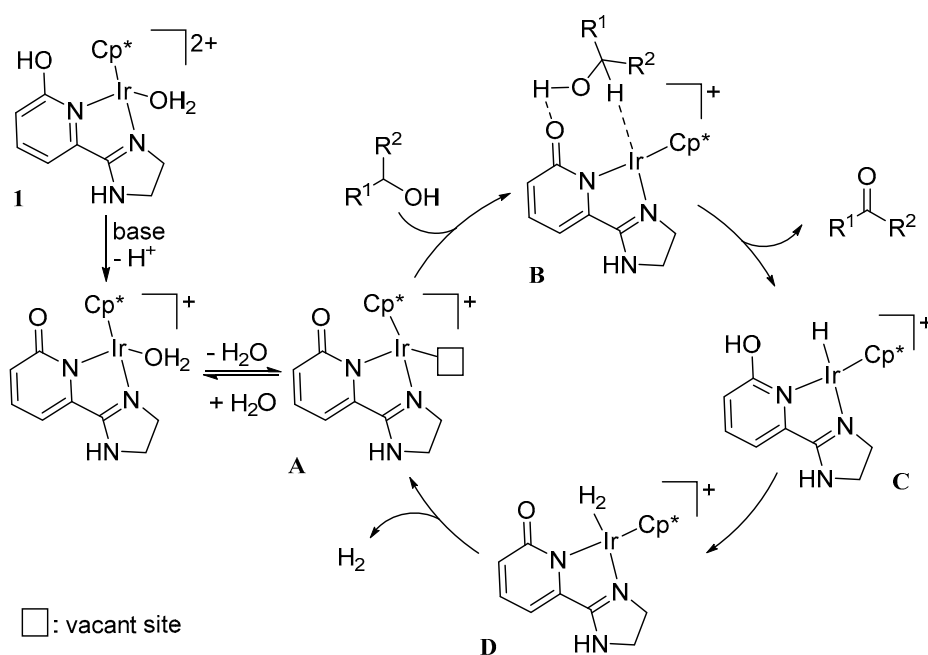
Table 3. Dehydrogenative oxidation of various secondary alcohols to the corresponding ketones catalyzed by **1** in aqueous media.



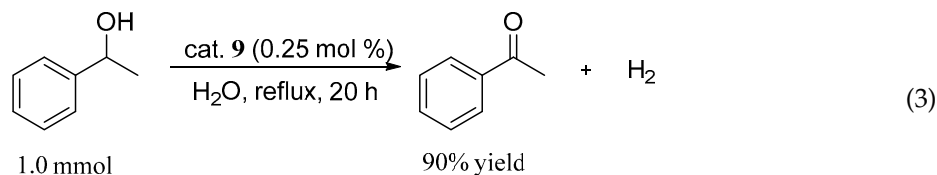
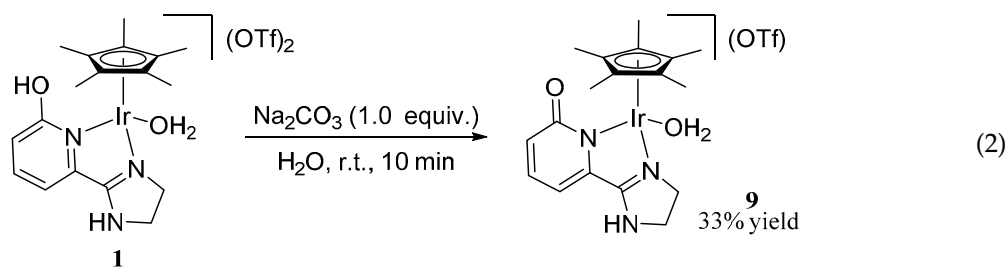
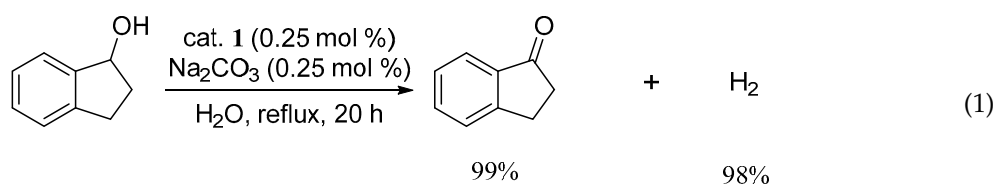
Yields were determined by ¹H NMR analysis. Isolated yields are shown in the parentheses. ^a 1.0 mol % of complex **1** and Na₂CO₃ were used as catalyst. ^b Reaction time was 72 h.

A possible mechanism for the dehydrogenative oxidation of alcohols catalyzed by **1** is depicted in Scheme 1. Firstly, the base-promoted elimination of triflic acid along with the dissociation of aquo ligand from catalyst **1** would occur to generate a monocationic coordinatively unsaturated species **A** having an α -pyridonate moiety connected to the 4,5-dihydro-1*H*-imidazol-2-yl unit. Further, activation of the alcohol substrate would occur through transition state **B** which produces the ketonic product with the concomitant formation of iridium hydride species **C**. The final step would involve the protonolysis of the hydride on the iridium center by the hydroxy proton on the functional ligand, regenerating the catalytically active unsaturated species **A** along with release of hydrogen gas.

To verify the possible mechanism, some experiments were carried out. First, a quantitative analysis of the evolved hydrogen gas was conducted (Equation (1)). When the dehydrogenative oxidation of 1-indanol in aqueous media on a large scale (10 mmol scale) was performed, hydrogen gas was obtained in 98% yield, which was almost equimolar amount to that of the ketone product (99%). The second experiment addressed the formation of the catalytically active monocationic species **A** (Equation (2)). By the treatment of the dicationic catalyst **1** with one equivalent of Na₂CO₃ at room temperature for 10 min, a new monocationic complex **9** having an α -pyridonate ring connected to the 4,5-dihydro-1*H*-imidazol-2-yl moiety, which is closely related to the species **A** in Scheme 1, was isolated in 33% yield. The structure of **9** was determined by spectroscopic data (see the Supplementary Materials). Further, the catalytic performance of **9** was investigated (Equation (3)). As expected, the complex **9** showed high catalytic activity for the dehydrogenation of 1-phenylethanol in water with a loading of 0.25 mol % even in the absence of base to give acetophenone in a high yield (90%). We assume that the results of these reactions (Equations (1)–(3)) strongly support the proposed catalytic cycle that is depicted in Scheme 1.



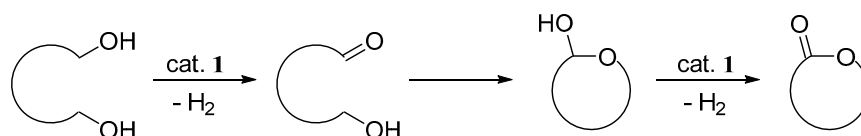
Scheme 1. Possible mechanism of the present dehydrogenative oxidation of alcohols catalyzed by **1**.



As a further application of the dehydrogenative oxidation system catalyzed by **1**, we examined the dehydrogenation of diols in water. Although we have previously reported a similar catalytic system for the dehydrogenative lactonization using a water-soluble iridium catalyst having a bipyridine-based functional ligand, a relatively high catalyst loading (1.0–3.0 mol %) was required in those cases [10]. Therefore, in this study, we attempted the reactions of various diols using 0.25 mol % of catalyst **1** and Na_2CO_3 . The results are summarized in Table 4. A variety of lactones having five- or six-membered ring structures could be obtained in good to excellent yields by conducting the reactions in aqueous media. For the substrates depicted in entries 5–7, two isomers of lactones were obtained. In those

cases, each product was isolated as a mixture of isomers, the ratios of which were determined by ^1H NMR analysis.

The reaction pathway for dehydrogenative lactonization is illustrated in Scheme 2. In the first step, one of the alcohol moieties in the diol substrate would be transformed to the aldehyde by catalytic dehydrogenation. Then, an intramolecular cyclization would afford the corresponding hemiacetal. Finally, dehydrogenative transformation would occur to generate lactone as a product.



Scheme 2. Reaction pathway for the dehydrogenative lactonization catalyzed by 1.

Table 4. Dehydrogenative lactonization of diols in aqueous media catalyzed by 1.

entry	diol	product	yield (%) ^a
1			98 (81)
2 ^b			98 (91)
3			78 (73)
4			99 (71)
5 ^{b,c}			91, 82 : 18 ^d (91, 82 : 18 ^d)
6			99, 48 : 52 ^d (86, 47 : 53 ^d)
7			98, 45 : 55 ^d (88, 48 : 52 ^d)

^a Yields were determined by ^1H NMR analysis. Isolated yields are shown in parentheses. ^b 0.5 mol % of complex 1 and Na_2CO_3 were used as catalyst. ^c Reaction time was 48 h. ^d Ratio of two isomers.

3. Experimental Section

3.1. General

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded on ECX-500 and ECS-400 spectrometers (JEOL, Akishima, Tokyo, Japan) at room temperature. Gas chromatography (GC) analyses were performed on a GC353B gas chromatograph (GL-Sciences, Shinjuku, Tokyo, Japan) with a capillary column [InertCap Pure WAX (GL-Sciences, Shinjuku, Tokyo, Japan)]. Elemental analyses were carried out at the Microanalysis Center of Kyoto University. Silica-gel column chromatography was carried out using Wako-gel C-200 (FUJIFILM Wako Pure Chemical Corporation, Doshoumachi, Osaka, Japan). The compounds, $[\text{Cp}^*\text{IrCl}_2]_2$ ($\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$) [25] and $[\text{Cp}^*\text{Ir}(\text{OH}_2)_3](\text{OTf})_2$ [26] were prepared according to the literature method. The diol **7b** was prepared by the reduction of 2-benzoylbenzoic acid using LiAlH_4 [10]. The diols **7e–g** were prepared by the reduction of the corresponding dicarboxylic acids using $\text{BH}_3\text{-THF}$ [10]. All other reagents are commercially available and were used as received.

3.2. Preparation of Dicationic Complexes 1–4

In a two-necked round-bottomed flask under argon atmosphere, $[\text{Cp}^*\text{Ir}(\text{OH}_2)_3](\text{OTf})_2$ (1.14 g, 1.68 mmol), 2-(4,5-dihydro-1H-imidazol-2-yl)-6-methoxymethoxypyridine (348 mg, 1.68 mmol), and degassed distilled water (10 mL) were placed. The mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the mixture was washed with CH_2Cl_2 (15 mL \times 3) and Et_2O (10 mL \times 1). Evaporation of the water layer under vacuum gave a crude product of complex **1** as a yellow powder. The product was purified by recrystallization from water (orange crystals, 965 mg, 1.20 mmol, 71%).

Analysis: ^1H NMR (400 MHz, methanol- d_4): δ 8.13 (t, $J = 7.2$ Hz, 1H, aromatic), 7.63 (d, $J = 7.2$ Hz, 1H, aromatic), 7.33 (d, $J = 8.0$ Hz, 1H, aromatic), 4.34 (t, $J = 10$ Hz, 2H, $-\text{N}(\text{CH}_2)-$), 4.10 (t, $J = 11$ Hz, 2H, $-\text{N}(\text{CH}_2)-$), 1.77 (s, 15H, Cp^*). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, methanol- d_4): δ 173.2, 165.6, 144.9, 144.8, 123.3 (q, CF_3), 118.2, 117.4, 89.6, 53.8, 47.0, 9.7. ^1H NMR (500 MHz, D_2O): δ 7.97 (dd, $J = 8.0$ Hz, 7.0 Hz, 1H, aromatic), 7.42 (d, $J = 7.0$ Hz, 1H, aromatic), 7.23 (d, $J = 8.0$ Hz, 1H, aromatic), 4.27 (t, $J = 10.5$ Hz, 2H, $-\text{N}(\text{CH}_2)-$), 4.02 (t, $J = 10.5$ Hz, 2H, $-\text{N}(\text{CH}_2)-$), 1.70 (s, 15H, Cp^*). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, D_2O): δ 172.5, 165.0, 144.1, 143.5, 120.3 (q, $J_{\text{CF}} = 316$ Hz), 117.2, 117.1, 88.6, 53.1, 46.4, 9.27. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_3\text{O}_8\text{IrF}_6\text{S}_2$: C, 29.78; H, 3.25; N, 5.21. Found: C, 29.42; H, 3.25; N, 5.14.

Complexes **2–4** were prepared by the similar procedures for complex **1**.

Complex **2** (61%): Analysis: ^1H NMR (400 MHz, methanol- d_4): δ 8.15 (t, $J = 8.0$ Hz, 1H, aromatic), 7.92 (d, $J = 8.0$ Hz, 1H, aromatic), 7.35 (d, $J = 8.0$ Hz, 1H, aromatic), 4.20 (m, 4H, $-\text{N}(\text{CH}_2\text{CH}_2)\text{N}-$), 3.50 (s, 3H, NCH_3), 1.75 (s, 15H, Cp^*). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, methanol- d_4): δ 171.3, 165.7, 144.9, 144.8, 123.3, 120.0, 117.4, 89.8, 56.7, 51.9, 35.7, 9.8. Anal. Calcd for $\text{C}_{21}\text{H}_{29}\text{N}_3\text{O}_8\text{IrF}_6\text{S}_2 \cdot 2\text{H}_2\text{O}$: C, 29.40; H, 3.88; N, 4.90. Found: C, 29.50; H, 3.62; N, 4.92.

Complex **3** (75%): Analysis: ^1H NMR (400 MHz, methanol- d_4): δ 9.24 (d, $J = 5.2$ Hz, 1H, aromatic), 8.45 (t, $J = 7.6$ Hz, 1H, aromatic), 8.23 (d, $J = 7.6$ Hz, 1H, aromatic), 8.02 (t, $J = 6.4$ Hz, 1H, aromatic), 4.38 (t, $J = 10$ Hz, 2H, $-\text{N}(\text{CH}_2)-$), 4.18 (t, $J = 11$ Hz, 2H, $-\text{N}(\text{CH}_2)-$), 1.80 (s, 15H, Cp^*). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, methanol- d_4): δ 172.5, 154.3, 148.0, 143.2, 132.1, 126.8, 123.3, 89.8, 53.6, 47.4, 9.12. Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{N}_3\text{O}_7\text{IrF}_6\text{S}_2$: C, 30.38; H, 3.31; N, 5.31. Found: C, 30.29; H, 3.32; N, 5.27.

Complex **4** (88%): Analysis: ^1H NMR (400 MHz, methanol- d_4): δ 8.36 (t, $J = 7.6$ Hz, 1H, aromatic), 7.80 (d, $J = 1.2$ Hz, 1H, aromatic), 7.69 (d, $J = 9.2$ Hz, 1H, aromatic), 4.36 (m, 2H, $-\text{N}(\text{CH}_2)-$), 4.13 (m, 2H, $-\text{N}(\text{CH}_2)-$), 4.34 (s, 3H, OCH_3), 1.76 (s, 15H, Cp^*). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, methanol- d_4): δ 173.1, 165.9, 146.2, 145.7, 123.4, 119.4, 114.4, 89.9, 59.1, 54.0, 47.1, 9.8. Anal. Calcd for $\text{C}_{21}\text{H}_{28}\text{N}_3\text{O}_8\text{IrF}_6\text{S}_2 \cdot 2\text{H}_2\text{O}$: C, 29.44; H, 3.76; N, 4.90. Found: C, 29.72; H, 3.73; N, 4.84.

3.3. General Procedures for the Dehydrogenative Oxidation of 1-Phenylethanol (Tables 1 and 2)

In a flask under argon atmosphere, catalyst **1** (0.0025 mmol, 0.25 mol %), 1-phenylethanol (1.0 mmol), degassed distilled water (3.0 mL) and 0.1 M Na_2CO_3 aq. (25 μL) were placed. The mixture

was stirred under reflux for 20 h in an oil bath (135 °C). After cooling to room temperature, the mixture was diluted with THF (10 mL). The conversion of 1-phenylethanol and the yield of acetophenone were determined by GC analysis using biphenyl as an internal standard.

3.4. General Procedure for the Dehydrogenative Oxidation of Secondary Alcohols (Table 3)

In a flask under argon atmosphere, catalyst **1** (0.0025 mmol, 0.25 mol %), secondary alcohol (1.0 mmol), degassed distilled water (3.0 mL) and 0.1 M Na₂CO₃ aq. (25 µL, 0.0025 mmol, 0.25 mol %) were placed. The mixture was stirred under reflux for 20 h in an oil bath (135 °C). After cooling to room temperature, the produced ketones were isolated by column chromatography on silica-gel (eluent: hexane/ethyl acetate).

4'-Methylacetophenone (6b) [27]: ¹H NMR (400 MHz, CDCl₃): δ 7.87 (m, 2H, aromatic), 7.26 (m, 2H, aromatic), 2.58 (s, 3H, -COCH₃), 2.41 (s, 3H, -CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 197.8, 143.8, 134.7, 129.2, 128.4, 26.5, 21.6.

4'-Methoxyacetophenone (6c) [28]: ¹H NMR (400 MHz, CDCl₃): δ 7.95 (m, 2H, aromatic), 6.93 (m, 2H, aromatic), 3.87 (s, 3H, OCH₃), 2.56 (s, 3H, -COCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 196.8, 163.5, 130.6, 130.3, 114.0, 55.5, 26.3.

4'-(N,N-dimethylamino)acetophenone (6d) [27]: ¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 6.8 Hz, 2H, aromatic), 6.64 (m, 2H, aromatic), 3.03 (s, 6H), 2.49 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 196.4, 153.4, 130.5, 125.1, 110.6, 40.0, 26.0.

4'-Trifluoromethylacetophenone (6e) [29]: ¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, *J* = 8.4 Hz, 2H, aromatic), 7.71 (d, *J* = 7.6 Hz, 2H, aromatic), 2.63 (s, 3H, -COCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 197.1, 139.8, 134.4 (q, *J*_{CF} = 32.4 Hz), 128.7, 125.8 (d, *J*_{CF} = 2.8 Hz), 123.7 (q, *J*_{CF} = 271.8 Hz), 26.9.

4'-Fluoroacetophenone (6f) [29]: ¹H NMR (400 MHz, CDCl₃): δ 7.94 (m, 2H, aromatic), 7.08 (t, *J* = 8.8 Hz, 2H, aromatic), 2.54 (s, 3H, -COCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 196.5, 165.8 (d, *J*_{CF} = 253.6 Hz), 133.6, 131.0 (d, *J*_{CF} = 8.5 Hz), 115.6 (d, *J*_{CF} = 21.9 Hz), 26.5.

4'-Chloroacetophenone (6g) [30]: ¹H NMR (400 MHz, CDCl₃): δ 7.89 (ddd, *J* = 8.4, 2.4, 1.6 Hz, 2H, aromatic), 7.42 (dt, *J* = 8.8, 2.0 Hz, 2H, aromatic), 2.59 (s, 3H, -COCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 196.7, 139.6, 135.5, 129.6, 128.9, 26.6.

3'-Methylacetophenone (6h) [31]: ¹H NMR (400 MHz, CDCl₃): δ 7.75 (m, 2H, aromatic), 7.33 (m, 2H, aromatic), 2.57 (s, 3H, -COCH₃), 2.40 (s, 3H, -CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 198.4, 138.3, 137.1, 133.9, 128.8, 128.4, 125.6, 26.7, 21.3.

3'-Methoxyacetophenone (6i) [28]: ¹H NMR (400 MHz, CDCl₃): δ 7.50 (m, 1H, aromatic), 7.45 (m, 1H, aromatic), 7.33 (m, 1H, aromatic), 7.07 (m, 1H, aromatic), 3.81 (s, 3H, -OCH₃), 2.56 (s, 3H, -COCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 197.9, 159.8, 138.5, 129.6, 121.1, 119.6, 112.4, 55.4, 26.7.

3'-Chloroacetophenone (6j) [31]: ¹H NMR (400 MHz, CDCl₃): δ 7.88 (m, 1H, aromatic), 7.79 (m, 1H, aromatic), 7.49 (m, 1H, aromatic), 7.37 (t, *J* = 8.0 Hz, 1H, aromatic), 2.56 (s, 3H, -COCH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 196.8, 138.6, 134.9, 133.1, 130.0, 128.4, 126.5, 26.7.

1-Indanone (6k) [32]: ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.6 Hz, 1H, aromatic), 7.54 (m, 1H, aromatic), 7.44 (m, 1H, aromatic), 7.32 (m, 1H, aromatic), 3.09 (t, *J* = 6.0 Hz, 2H), 2.70–2.63 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 207.0, 155.2, 137.2, 134.6, 127.2, 126.7, 123.6, 36.2, 25.8.

α-Tetralone (6l) [32]: ¹H NMR (400 MHz, CDCl₃): δ 8.01 (m, 1H, aromatic), 7.45 (m, 1H, aromatic), 7.32–7.18 (m, 2H, aromatic), 2.92 (m, 2H), 2.61 (m, 2H), 2.07 (m, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 198.1, 144.4, 133.2, 132.9, 128.7, 126.9, 126.4, 39.0, 29.5, 23.1.

Propiophenone (6m) [31]: ¹H NMR (400 MHz, CDCl₃): δ 7.95 (m, 2H, aromatic), 7.52 (m, 1H, aromatic), 7.43 (m, 2H, aromatic), 2.99 (q, *J* = 7.2 Hz, 2H, CH₂CH₃), 1.21 (t, *J* = 7.2 Hz, 3H, CH₂CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 200.8, 136.9, 132.9, 128.6, 128.0, 31.8, 8.3.

3.5. Procedure for the Quantitative Analysis of the Evolved Hydrogen Gas in the Dehydrogenative Oxidation of 1-Indanol (Equation (1))

In a flask connected with a gas burette through a condenser under argon atmosphere, catalyst **1** (20.3 mg, 0.025 mmol), distilled water (30 mL), 0.1 M Na₂CO₃ aq. (250 µL) and 1-indanol (1.35 g, 10 mmol) were placed. The mixture was stirred under reflux for 20 h in an oil bath (135 °C). The yield of 1-indanone was determined by ¹H NMR (CDCl₃) using triphenylmethane as an internal standard. The volume of evolved gas was measured by a gas burette. The molar amount of hydrogen was calculated using the ideal gas law. The purity of evolved hydrogen gas was confirmed by GC analysis (experimental detail is described in the Supplementary Materials).

3.6. Preparation of Monocationic Complex **9** (Equation (2))

In a flask under argon atmosphere, complex **1** (101.6 mg, 0.126 mmol) was placed. 0.1 M Na₂CO₃ aq. (1.25 mL) was added and stirred for 10 min at room temperature. Then, the solvent water was evaporated by the vacuum pump and the deposited dark green powder remained. The powder was dissolved in dry CH₂Cl₂ and filtered by Celite under argon atmosphere. The filtrate organic layer was washed by distilled water (10 mL × 4) under argon atmosphere, then the solvent was removed by evaporation and the dark green powder was obtained (27.2 mg, 0.041 mmol, 33%). Results of the NMR analysis of complex **9** are shown in the Supplementary Materials.

3.7. General Procedure for the Dehydrogenative Lactonization of Diols (Table 4)

In two-necked test tube under argon atmosphere, catalyst **1** (0.0025 mmol, 0.25 mol %), diol (1.0 mmol), distilled water (1.5 mL) and 0.1 M Na₂CO₃ aq. (25 µL, 0.0025 mmol, 0.25 mol %) were placed. The mixture was stirred under reflux for 20 h in an oil bath (135 °C). After cooling to room temperature, the solvent was evaporated. The yield of the product was determined by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The product was isolated by silica-gel column chromatography (eluent: hexane/ethyl acetate).

Phthalide (8a) [33]: ¹H NMR (500 MHz, CDCl₃): δ 7.91 (d, *J* = 7.5 Hz, 1H, aromatic), 7.71 (td, *J* = 7.5, 1.0 Hz, 1H, aromatic), 7.56–7.52 (m, 2H, aromatic), 5.34 (s, 2H, -CH₂-). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 171.2, 146.6, 134.1, 129.0, 125.6, 125.6, 122.2, 69.7.

3-Phenyl-1(3H)-isobenzofuranone (8b) [34]: ¹H NMR (500 MHz, CDCl₃): δ 7.97 (d, *J* = 7.5 Hz, 1H, aromatic), 7.66 (t, *J* = 7.5 Hz, 1H, aromatic), 7.56 (t, *J* = 7.5 Hz, 1H, aromatic), 7.41–7.36 (m, 3H, aromatic), 7.34 (d, *J* = 7.5 Hz, 1H, aromatic), 7.30–7.27 (m, 2H, aromatic). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 170.7, 149.8, 136.5, 134.5, 129.5, 129.4, 129.1, 127.1, 125.8, 125.7, 123.0, 82.9.

Naphtho[2,3-*c*]furan-1(3H)-one (8c) [33]: ¹H NMR (400 MHz, CDCl₃): δ 8.52 (s, 1H, aromatic), 8.06 (d, *J* = 8.4 Hz, 1H, aromatic), 7.96 (d, *J* = 8.4 Hz, 1H, aromatic), 7.92 (s, 1H, aromatic), 7.67 (td, *J* = 6.8, 1.2 Hz, 1H, aromatic), 7.61 (t, *J* = 8.0 Hz, 1H, aromatic), 5.5 (s, 2H, -CH₂-). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 171.1, 140.1, 136.3, 133.2, 130.0, 129.1, 128.2, 127.1, 127.1, 123.5, 120.1, 69.8.

1H,3H-Naphtho[1,8-*cd*]pyran-1-one (8d) [33]: ¹H NMR (400 MHz, CDCl₃): δ 8.35 (dd, *J* = 7.6, 0.8 Hz, 1H, aromatic), 8.08 (d, *J* = 8.0 Hz, 1H, aromatic), 7.81 (d, *J* = 8.4 Hz, 1H, aromatic), 7.62 (dd, *J* = 8.0, 7.2 Hz, 1H, aromatic), 7.53 (t, *J* = 7.2 Hz, 1H, aromatic), 7.34 (dd, *J* = 7.2, 0.8 Hz, 1H, aromatic), 5.79 (s, 2H, -CH₂-). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 170.3, 139.0, 137.3, 132.7, 131.9, 130.7, 130.2, 128.8, 128.7, 128.6, 128.5, 69.2.

3,4-Dihydro-1H-2-benzopyran-1-one (8ea) [35], **1,4-Dihydro-3H-2-benzopyran-3-one (8eb)** [36]: ¹H NMR (500 MHz, CDCl₃): δ 8.08 (dd, *J* = 6.4, 0.8 Hz 1H), 7.55 (td, *J* = 6.0, 1.2 Hz, 1H), 7.41 (t, *J* = 6.0 Hz, 1H), 7.27 (m, 1H), 4.55 (t, *J* = 4.8 Hz, 2H), 3.08 (t, *J* = 4.8 Hz, 2H). ¹³C{¹H} NMR (125 MHz, CDCl₃): δ 165.0, 139.5, 133.6, 130.1, 127.5, 127.2, 125.1, 67.2, 27.6. ¹H NMR (400 MHz, CDCl₃): δ 7.37–7.23 (m, 4H), 5.32 (s, 2H), 3.72 (s, 2H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 170.7, 131.5, 130.9, 128.6, 126.9, 124.5, 69.9, 36.1.

6-Methyl-1(3H)-isobenzofuranone (8fa) [33], **5-Methyl-1(3H)-isobenzofuranone (8fb)** [33]: ¹H NMR (500 MHz, CDCl₃): δ 7.70 (s, 1H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 5.27 (s, 2H), 2.50 (s,

3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 171.2, 143.8, 139.1, 135.1, 125.6, 125.3, 121.8, 69.6, 21.1. ^1H NMR (500 MHz, CDCl_3): δ 7.79 (d, J = 8.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.29 (s, 1H), 5.29 (s, 2H), 2.47 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 171.1, 147.1, 145.2, 130.0, 125.3, 122.9, 122.4, 69.4, 21.9.

6-Fluoro-1(3H)-isobenzofuranone (8ga) [37]: ^1H NMR (500 MHz, CDCl_3): δ 7.58 (dd, J = 2.5, 7.0 Hz, 1H, aromatic), 7.49 (m, 1H, aromatic), 7.42 (td, J = 2.5, 8.5 Hz, 1H, aromatic), 5.32 (s, 2H, $-\text{CH}_2-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 170.1 (d, J_{CF} = 3.5 Hz), 163.2 (d, J_{CF} = 248.0 Hz), 142.0, 127.9 (d, J_{CF} = 9.6 Hz), 123.9 (d, J_{CF} = 8.4 Hz), 122.2 (d, J_{CF} = 23.9 Hz), 112.3 (d, J_{CF} = 23.9 Hz), 69.6 (s).

5-Fluoro-1(3H)-isobenzofuranone (8gb) [37]: ^1H NMR (500 MHz, CDCl_3): δ 7.93 (dd, J = 8.5, 5.0 Hz, 1H, aromatic), 7.25 (td, J = 8.8, 2.0 Hz, 1H, aromatic), 7.20 (dd, J = 7.5, 1.5 Hz, 1H, aromatic), 5.32 (s, 2H, $-\text{CH}_2-$). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3): δ 170.0, 166.7 (d, J_{CF} = 255.1 Hz), 149.4 (d, J_{CF} = 10.8 Hz), 128.2 (d, J_{CF} = 9.5 Hz), 122.0, 117.5 (d, J_{CF} = 23.8 Hz), 109.6 (d, J_{CF} = 23.9 Hz), 69.1 (d, J_{CF} = 3.6 Hz).

4. Conclusions

In summary, we have synthesized water-soluble and stable dicationic complexes 1–4 having a bidentate functional ligand that comprises substituted or non-substituted pyridine and 4,5-dihydro-1H-imidazol-2-yl moieties. Among the prepared complexes, derivative 1, which contained an α -hydroxypyridine in the functional ligand, exhibited high catalytic performance in the dehydrogenative oxidation of secondary alcohols to the corresponding ketones in aqueous media. Furthermore, the complex 1 also exhibited high catalytic activity for the dehydrogenative lactonization of diols in aqueous media. For both reactions, lower catalyst loadings were required as compared to the requirement of the previously reported systems.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/8/8/312/s1>. Figure S1. Reaction setup for the quantitative analysis of the evolved hydrogen gas. Figure S2. GC analyses of the hydrogen gas. a) The chromatogram of the evolved gas by the reaction of 1-indanol. b) The chromatogram of the standard gas of pure hydrogen. Figure S3. ^1H NMR(D_2O) experiment for detection of the active species.

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